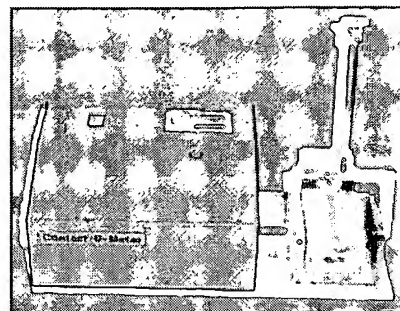


Surface Energy and Contact Angle Measurements on Solids

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Scope and Field of Application

The techniques described on this page are the ones that are used to measure the properties of solids (i.e. the surfaces of substrates or of dry coatings). If you are more interested in the properties of liquids, then please visit our Surface Tension and Contact Angle Measurements on Liquids page.

The end product of any successful painting or printing process is normally a dry film of the coating on a substrate. In cases where liquid paints or inks are applied, an essential intermediate stage in the process is the formation of a satisfactory wet film of the coating.

The success or otherwise of producing a satisfactory wet film depends on both the properties of the liquid coating and the properties of the substrate.

It is probably helpful to define the relevant properties that we are able to measure:-

Surface Tension

The origin of surface tension in a liquid is the forces of attraction between the molecules that make up the liquid. In the absence of other forces, this mutual attraction of the molecules caused the liquid to coalesce to form spherical droplets. This can be seen, for example, when rain falls on a freshly waxed car body.

As a general rule, the greater the proportion of polar groups (e.g O-H groups) in a molecule the stronger the attractive forces between them. Strong attractive forces give rise to a high surface tension and a tendency to form discrete droplets on a surface rather than wet it evenly. The large proportion of O-H groups in water are responsible for its high surface tension. Alcohols, with their smaller proportion of O-H groups, have lower surface tensions.

Clearly, all things being equal, the lower the surface tension of a liquid coating, the easier it will be to form a satisfactory wet film from it.

Surface tension can be thought of as the force that holds a liquid together. In the depths of a volume of liquid, each molecule is surrounded on all sides by other molecules; the forces between them balance out and the entire mass is in equilibrium. The situation is different at the surface of a liquid. At a liquid-air interface for example, the molecules at the surface are being attracted by the surrounding liquid but not by the air. The forces are imbalanced and consequently the liquid behaves as if had a stretched skin.

Surface tension can therefore be quantified in terms of the forces acting on a unit length at the liquid-air interface. The units are dynes per centimetre or newtons per metre (1 dyne per centimetre is equal to 1 milli-newton per metre)

Surface Energy

How can a surface have energy? At first sight this is not an unreasonable question. Energy is defined as the capacity to do work and if we take the example of the average wooden desk top it is difficult to find evidence that it is engaged in any form of work.

The situation becomes clearer when we spray water droplets on a desk top, part of which has been wax polished. The droplets that land on the polished areas will form discrete near-spherical droplets. This is due to the surface tension of the water (see above).

The water droplets that land on the un-polished wood behave differently. They tend not to form droplets but to spread out to form a thin film. In other words the surface tension forces that hold the water droplets together have been overcome. It takes energy to overcome the surface tension forces and this energy has to come from somewhere. In fact it comes from the surface of the desktop and more specifically from the forces that hold the molecules of the desktop material together.

A desktop which has been polished using a hydrocarbon wax will have a surface rich in hydrocarbon molecules. The forces that hold hydrocarbons together are much weaker than the forces that act between water molecules and consequently water on a hydrocarbon surface remains in the droplet form.

An un-polished wood surface will have at its surface a complex mixture of molecules made from carbon hydrogen and oxygen and (unlike hydrocarbons) there will be a significant proportion of polar groups (e.g. O-H) present. The forces of attraction between polar molecules are stronger than those between non-polar hydrocarbon molecules and in this example they are sufficiently strong to overcome the surface tension forces of water and cause the droplets to spread out and form a film.

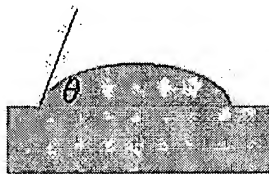
It is common in the coatings industry to refer to **low energy** and **high energy** surfaces. Polyethylene and polypropylene are examples of low energy surfaces. The forces between the hydrocarbon molecules that make up the polymers are weak and consequently polar liquids tend to form droplets on the surface rather than spread out.

It is difficult to coat low energy surfaces but fortunately there are numerous ways of converting low energy into high energy surfaces. All the methods aim to form oxygen containing species at the surface and this oxidation can be achieved by exposure to ultraviolet radiation, plasma or corona discharge or by flame or acid treatment.

Surface energy is quantified in terms of the forces acting on a unit length at the solid-air or the solid-liquid interface. The units of measurement are exactly the same as for surface tension.

Contact Angle

The definitions of surface tension and surface energy have involved consideration of the behaviour of liquids in contact with solids and the formation of droplets or thin films. One convenient way of quantifying this behaviour is to measure the angle θ formed by the liquid-solid and the liquid-liquid interfaces:-



If θ is greater than 90° the liquid tends to form droplets on the surface. If θ is less than 90° the liquid tends to spread out over the surface and when the liquid forms a thin film, θ tends to zero.

Adhesion

There are several methods of quantifying the adhesion of a coating to a substrate and these are described on our Adhesion Testing page. Although none of these methods requires a fundamental understanding of the mechanism of adhesion, it is appropriate to mention it here because surface tension, surface energy and adhesion are all interrelated.

The numerical difference between the surface tension of a coating and the surface energy of a substrate has a profound effect on the way in which the liquid coating flows out over the substrate and on the strength of the adhesive bond between the substrate and the dry film.

If the surface tension of the coating is greater than the surface energy of the substrate then the coating will not spread out and form a film. As we increase the surface energy we can reach a stage where the coating will spread out and form a film but, when dry, has poor adhesion. Further increases in the surface energy will result in easier wet-film formation and better dry-film adhesion.

It is important to emphasise that surface energy is only one aspect governing the complex phenomenon that we refer to as adhesion. Adhesive testing involves the application of force to remove the coating from the substrate. The intention is to measure the force needed to overcome the forces of adhesion between coating and substrate. In practice however, the cohesive strength of the coating and of the substrate both have an effect on how easy it is to remove the coating. In fact there is a supportable case for saying that there is no such thing as a true adhesive failure since, at the molecular level, all failures are cohesive failures of the coating or the substrate.

Summary of Methods

Measurement of Surface Energy

We offer three in-house methods for measuring surface energy. The dyne pen and the contact meter methods can be used on any surface while the interfacial tensiometer can only be used on a homogenous non-porous solid.

Dyne Pen Method

This involves the use of a set of commercially available felt-tip pens containing a range of inks of known surface tension. One of the pens is used to apply a thin film of ink over about 7 square centimetres of the test surface. If the ink film breaks up into droplets in less than two seconds, the process is repeated using a pen filled with ink having a lower surface tension. This procedure is used to establish the lowest surface tension ink that will yield a film that remains intact for at least two seconds. The value of the surface tension of this ink is then taken as the surface energy of the test substrate.

Contact Angle Meter Method

In this method, a drop of a liquid of known surface tension is placed on the test surface, illuminated and then viewed through a moveable eyepiece. The eyepiece is connected to an electronic protractor which displays the viewing angle.

The meter is constructed so that when the viewing angle equals the contact angle, the illumination viewed through the eyepiece is maximised. The contact angle and the surface tension of the liquid can then be used to calculate the surface energy of the substrate.

This is not the most accurate method of measuring contact angles and we only recommend it in cases where you wish to determine the contact angle of a coating applied to only one side of a substrate. If your sample is coated on all sides (and does not require cutting to size) or if it is uncoated with each face having the same composition (e.g. a piece of polymer) then you should consider the tensiometer method described on our Surface Tension and Contact Angle Measurements on Liquids page.

Interfacial Tensiometer Method

We use a Camtel CDCA-100 instrument which is a versatile computer controlled tensiometer capable of measuring surface tensions and contact angles and calculating surface energies.

The method involves dipping the solid into and retracting it from a liquid of known surface tension. The variation of contact angle with immersion depth is measured and these values are used by the in-built software to calculate the surface energy of the solid.

Sample Requirements

Surface energy measurements can be carried out on substrates or on dry coatings using either the dyne pen or the contact meter method. The tensiometer method is restricted to solids where all exposed faces have the same composition. If you wish, we can prepare the test pieces. The quantity of liquid paint we needs depends on the method of application. We will be pleased to advise you regarding our requirements.

Dyne Pen Method

This can be carried out on any surface with minimum area of 50 square centimetres

Contact Angle Meter Method

We need a panel from which we can cut a test piece 20 x 75 x less than 10 mm.

Interfacial Tensiometer Method

This method can only be carried on non-porous homogeneous solids. This rules out wood and also coatings applied to any substrate. It is the technique to use if you need to measure accurately (for example) the surface energy of a sample of polymer.

We need to be able to cut a test piece 20 x 30 x not more than 5 mm.

Accreditation

Although PRA is accredited to ISO 17025 by the United Kingdom Accreditation Service (UKAS), we are not accredited to carry out these tests.

Please contact Norman Falla for further details.

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